Conference report

Gold Highlights at NanoSpain Conference in Braga, Portugal April 14–18, 2008

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Most of 350 participants who attended this conference were from Portugal and Spain but some were from the United Kingdom, The Netherlands, Germany, France, Romania, Slovakia, USA, Japan, Brazil, and Venezuela. Gold-related subjects had a strong presence with 34 posters and 16 talks (three of them from invited speakers). Potential applications for the advances in the technology described are indicated here.

Nanobiotechnology/nanomedicine

Interactions between gold nanoparticles and biological species found in aqueous solutions are being used as a basis for the development of biosensors: the highlights are summarized below:

Elvira Fortunato (13N Associate Laborabory, Caparica, Portugal) had both oral and poster presentations on 'DNA detection using amorphous silicon sensors with gold nanoparticles'. Gold nanoparticles with thiol modified oligonucleotides complementary to DNA targets - Au-nanoprobes - were used to distinguish fully complementary from mismatched sequences; and another poster entitled: 'Optimization and characterization of amorphous/nanocrystalline biosensors for DNA detection using gold nanoparticles' described an innovative optoelectronic platform for the colorimetric detection of nucleic acids based on oligonucleotide-derivatized gold nanoparticles.

Irene Fernandez-Cuesta (National Centre of Microelectronics of Barcelona, Spain) presented a poster and an oral entitled 'Interdigitated nanoelectrodes for sensing: fabrication and characterization'. The whole chip was fabricated in gold onto a SiO_2/Si substrate and used to detect and quantify insulating nanoparticles.

Amongst other posters in this section, Gonçalo Doria, (New University of Lisbon, Portugal), had one on 'Revealing the mechanism of single nucleotide polymorphisms (SNPs) detection with gold nanoprobes by non-cross-linking aggregation'. This consisted of a colorimetric method based on the differential non-cross-linking aggregation of gold nanoparticles with thiol-modified oligonucleotides - Au nanoprobes - upon hybridization with a complementary DNA target.

Inês Gomes, from the same University, described 'Probing the surface properties of cytochrome C/gold nanoparticle complexes'. Spherical gold nanoparticles were prepared and coated with horse heart cytochrome C (HHCC) and yeast iso-1-cytochrome C (YCC). Results showed that these molecules can be used to control properties on the nanoscale for these bio-nanoprobes.

Pedro Paulo (Technical University of Lisbon, Portugal) had a poster on 'Individual detection of gold nanoparticles in liquid using photothermal correlation spectroscopy'. By combining photothermal microscopy with a heterodyne detection scheme the sensitivity for a Au single-particle detection with size down to 20 nm can be obtained.

Christian Sporer (University of Barcelona, Spain) described 'Novel anionophores for biosensor applications. Characterisation of imidazolium protophanes and cyclophanes on gold surfaces', which reported the results of surface deposition of amphiphilic imidazolium heterocyclophanes and protophanes on gold electrodes.

Adriano Ambrosi (Autonomous University of Barcelona, Spain) described: 'Gold nanoparticles as versatile labels for enhanced protein detection'. Nanoparticles were modified with a model anti-human IgG peroxidase-conjugated antibody (anti-human IgG-HRP). Optical sensitivity enhancement attributable to the use of Au nanoparticles as a multi-IgG-HRP carrier allows the amplification of the enzymatic signal, and high sensitivity in the direct electrochemical detection.

Gemma Aragay, from the same University, reported on 'Gold nanoparticles modification with intramolecular coordination ligands with interest for sensing applications'. This included synthesis and characterization of Au nanoparticles modified with intramolecular coordination ligands from the N-alkylaminopyrazole family and their potential applications for future optical and electrochemical sensing systems.

Salvador Alegret, from the same University, described 'Gold nanoparticles used in impedimetric genosensing of double-tagged Polymerase Chain Reaction (PCR) samples'. The double-tagged DNA was immobilized onto the electrode surface and the impedimetric signal was amplified using gold nanoparticles modified with Anti-Mouse IgG – gold antibody. Rapid and sensitive detection of PCR amplified samples of *Salmonella spp*, the most important pathogen affecting food safety, were achieved.

Raul Baltazar (University of Algarve, Portugal) had a poster on Au nanoparticles for biosensing applications. A biomolecule-mediated template assay for antibody-antigene recognition was developed, based on the controlled aggregation of biotinylated gold nanoparticles, induced by addition of streptavidin molecules to solution, to detect DNA sequences.

Rogério Rodrigues, from the same University, described 'Qualitative and quantitative analysis of biorecognition in piezoelectric biosensors'. Alkanethiols forming Self Assembled Monolayers (SAMs) on gold surfaces which were used in the development of recombinant antibody-based biosensors for potential use in HIV-1 infection monitoring.

Joan Comenge (Catalan Institute of Nanotechnology, Barcelona, Spain) had the poster 'Addressing the immune system: macrophages responses towards Au nanoparticle conjugates'. The latter were used as scaffolds for biomolecules to test the response of macrophage cells, which play key roles in the immune system. Au NP-peptides conjugates induced macrophage activation.

Briza Pérez, from the same Institute, described 'Nanostructurated biosensors for the analysis of phenolic compounds', dealing with a Au electrode modified with polyaniline for a tyrosinase-based biosensor.

Belén Díaz (University of Vigo, Spain) had a poster on 'Reactive oxygen species induction and cytotoxicity of inorganic nanoparticles in human cells', describing the interaction *in vitro* of Au/SiO_2 with different human peripheral blood cells (lymphocytes, monocytes, granulocytes and erythrocytes), mouse macrophages and several human tumour cell lines.

Verónica Martins (Technical University of Lisbon, Portugal) described the: 'Biological detection limit of a giant magnetoresistive-based biochip for pathogenic analysis'. Thiol-modified DNA oligos directly attached to the gold surface were used as biorecognition probes and the microbiological quality of water for human consumption was evaluated via the detection of waterborn pathogen microorganisms.

María Moros (Aragón Institute of Nanoscience Research, Zaragoza, Spain) reported on 'Cell response against water stable magnetic nanoparticles obtained by thermal decomposition procedure'. Magnetite nanoparticles were prepared and coated with a polymer shell to ensure water solubility. The magnetic core was coated with a thin gold shell. The influence of these nanoparticles on Hella cell line and human fibroblasts was assessed *in vitro*.

NanoChemistry and NanoCatalysis

Gold nanoparticles can be used to produce materials with useful physical and chemical properties, including catalysis.

Marta Mas-Torrent (Institute of Material Science of Barcelona, Spain) gave a talk on 'Self-assembly of polychlorotriphenylmethyl organic radicals on surfaces', describing the functionalisation of SiO_2 on Au(111), with polychlorotriphenylmethyl (PTM) radicals, to be used as a chemical and electrochemical redox switch with optical (absorption and fluorescence) and magnetic responses.

Miguel Monge (University de la Rioja, Spain) gave a talk and poster entitled 'Silver nanoparticles and gold metallodendrimers: from molecular precursors to nanomaterials'. The latter are based on polypropyleneimine (PPI) or polyamidoamine (PAMAM) dendrimers functionalized with peripheral PPh_2 groups that allow the coordination of Au(I) fragments. When the periphery of the dendrimer is grafted onto Au(I)-thiolate units luminescent metallodendrimers are obtained.

Roberto Otero (Autonomous University of Madrid, Spain) had both an oral and poster on '1D ZnO chains as the spinal cord of adsorbed metalloporphyrin nanotubes linked by water ligands', describing formation of long tube-like structures of self-assembled Zn-porphyrin nanotubes created by deposition of aquo(tetramesitylporphyrinato)zinc(II) (H_2O-ZnTMP) on Au(111), which were not found upon deposition on H_2TMP alone. DFT calculations were consistent with the experimental results.

The following posters illustrate possibilities for forthcoming applications:

Sónia Carabineiro (University of Porto, Portugal) described the 'Preparation of gold nanoparticles on several supports and their use for the oxidation of carbon monoxide'. TiO_2, ZnO, Fe_2O_3 and La_2O_3 were compared and Au was impregnated by the Double Impregnation (DIM)[1] and the Liquid Phase Reductive Deposition (LPRD)[2] methods. The most active catalysts were obtained with Au/TiO_2 prepared by LPRD.

Luis Molina (University of Valladolid, Spain) described 'Ab initio studies of direct propene epoxidation at oxide-supported gold clusters and nanoparticles'. The DFT study of the reaction at the Au/TiO_2 interfacial region suggested an easy formation of a strongly bound propene oxide species at the Au/TiO_2 interface. Preliminary results from other Au/oxide materials showed that the activity of gold for propene epoxidation is not specific to a particular oxide.

Adelaide Miranda (University of Porto, Portugal) had a presentation on 'Gold anisotropic nanoparticles: synthesis and characterization'. Gold nanotriangles of (length ~130 nm, 15-19 nm height) were obtained by the photocatalytic reduction of hydrogen tetrachloroaurate (III) by triethanolamine using Sn (IV) meso-tetra(N-Methyl-4pyridyl)porphine tetratosylate chloride as the photocatalyst, and CTAB as the capping agent, in an aqueous medium.

Pedro Quaresma, from the same University, presented a poster with the title 'Sonochemical formation of gold nuclei on magnetite nanoparticles and growth to a core-shell system'. An ultrasound mediated iterative addition of gold precursor and reducing agent was employed.

Manuel Alcami (Autonomous University of Madrid, Spain) presented 'Understanding the supramolecular self-assembly of the fullerene derivative phenyl-C61-butyric acid methyl ester (PCBM) on Au(111) surface. Theoretical calculations

were performed based on density functional theory (DFT), which showed that the surface plays a very minor role in the process at high coverage.

Nanometrology

Rob H. Bergmans (NMi Van Swinden Laboratorium B.V, The Netherlands) gave an invited talk on 'Nanometrology and its role in the development of nanotechnology'. It was very interesting to know that standards for Au nanoparticles are recently available from the National Institute of Standards & Technology, from the USA for 10, 30 and 60 nm sizes[3].

NanoFabrication

Juán de la Figuera (Autonomous University of Madrid, Spain) gave a talk and poster on 'Nanoscale periodicity in stripe-forming systems at high temperature - the Au/W(110) system'. Submonolayers of Au self-assemble on W(110) into monolayer-thick stripes of condensed-phase Au in coexistence with stripes of a Au adatom gas, along the [110] crystallographic direction.

Steve Reyntjens (FEI Company, Eindhoven, The Netherlands) gave a talk presented on 'Novel tools for nanoprototyping using dualbeam™ FIB/SEM'. A split-ring resonator consisting of a Au layer on a glass substrate was shown to have potential applications for nanotechnology fabrication.

NanoMaterials

Au nanoparticles have been useful in producing substances with various properties, for example, in transistors and superconducting materials.

Daisuke Fujita (National Institute for Materials Science, Japan) presented an invited talk on 'Low-dimensional surface nanostructures studied by Scanning Tunneling Microscopy'. The fabrication of homogeneous gold nanoclusters on SAMs of dithiol on Au(111)/mica substrate was reported[4].

Amongst the posters were the following:
Fabienne Gauffre (University of Toulouse, France) on 'New strategies of colloidal stabilization of nanoparticles for applications in aqueous media'. The production of water dispersible semiconducting Au was reported and an interesting example of cellular uptake of gold nanoparticles coated by triblock copolymers was shown.

Pedro Barquinha (13N Associate Laboratory, Caparica, Portugal) described: 'Gallium-Indium-Zinc oxide based thin-film transistors produced at room temperature'. An improvement on the electrical properties with annealing performed at the end was shown for Ti/Au electrodes, as mobility rose from 19 to 25 cm^2/Vs and turn-on voltage dropped from 4 to 2 V.

S. Ricart (Institute of Materials Science of Barcelona, Spain) presented 'Nanoparticles on $YBa_2Cu_3O_{7-\delta}$ superconducting thin films'. Nanocomposite thin film containing previously or simultaneously synthesized Au nanoparticles in the $YBa_2Cu_3O_{7-\delta}$ matrix were obtained using the Metal Organic Decomposition (MOD) approach.

Daniel Alegre (Institute of Microelectronics of Madrid, Spain) described 'Properties of single-crystalline ZnO nanodots and highly-textured ZnO films grown by electrochemistry', indicating the growth of these ZnO structures by one step electrodeposition, without further thermal treatment on a large area on Au/Si substrates.

NanoPhotonics and NanoOptics

Xavier Borrise (National Centre of Microelectronics of Barcelona, Spain) gave a talk on 'Plasmon confinement in V-groove waveguides fabricated by NanoImprint Lithography'. The process consists in the fabrication of the stamp in silicon, imprint it with polymethylmethacrylate (PMMA) and evaporate a 200 nm thick film of gold on the PMMA structures. Then a UV sensitive polymer (Ormocomp®,) is cast onto the gold and cured with UV light.

António García-Martín and Juan Bautista González-Díaz (Microelectronics Institute of Madrid, Spain) presented an oral and a poster, respectively with the titles: 'Magneto-plasmonic materials: tuning magneto-optics with plasmons' and 'Surface plasmon resonance effects on the magneto-optical response of noble metal-ferromagnet nanodisks'. The magneto-optical (MO) response of Au/Co/Au trilayered systems can be enhanced when its surface plasmon resonance is excited, enabling to develop new high sensitivity biosensors. Au/Co/Au nanodisks obtained from continuous Au/Co/Au films by colloidal lithography also exhibited optical and MO properties.

Sérgio Pereira (University of Aveiro, Portugal) talked about 'Controlled integration of nanocrystals on the surface of group III-nitride light-emitting epitaxial heterostructures' dealing with manipulation of Au nanocrystals (NCs) with sizes ranging from ~5-30 nm. A precise number of Au NCs can be incorporated on the surface of efficient light emitting devices.

Niek van Hulst (Institute of Photonic Sciences of Barcelona, Spain) gave a talk on 'Nanoantennas - Controlling single molecule excitation and emission'. Although aluminum is a relatively good electrical conductor in the optical regime, gold, although less of a conductor, displays stronger plasmon resonances with potentially stronger field enhancement for these materials.

Scanning Probe Microscopies (SPM)

Mervyn Miles (University of Bristol, UK) presented an invited talk entitled 'High speed AFM – contact & non-contact'. Beautiful images of Au surfaces were shown.

Daniel Maspoch (Catalan Institute of Nanotechnology, Barcelona, Spain) presented an oral on 'Dip-Pen Nanolithography: "Writing" molecules, biological entities and nanomaterials at the nanometer scale'. This technique has been used to pattern alkanethiol SAMs and create nanoarrays of fluorescein onto gold surfaces.

Simulation at the nanoscale

Helder Barbosa (University of Minho, Portugal) presented a poster with the title 'Simulation in organic nanoelectronics: from single molecule to thin film'. By using a quantum molecular dynamics method authors studied the electron transfer in a molecular device consisting of a single conjugated molecule (with and without spatial symmetry) bound to two gold electrodes.

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References

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